Conversion of a substrate carbon source to formic acid for carbon dioxide emission reduction utilizing series-stacked microbial fuel cells

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HIGHLIGHTS

► An MFC-stack-driven MEC is used to electro-reduce CO_2 to formic acid.
► The MFC-generated electricity is utilized in situ to reduce the MFC-produced CO_2.
► Formic acid at 4.27 mg L^{-1} h^{-1} is produced with a Faraday efficiency of 64.8%.

ARTICLE INFO

ABSTRACT

Carbon dioxide (CO_2) is now known to be a major cause of global warming, and the reduction of its atmospheric concentration has therefore become a critical issue. The amount of CO_2 discharged from the degradation process of waste organic substances is both tremendous and neglected. Here, an environmentally friendly method to achieve the fixation of the CO_2 released from the degradation of waste carbonaceous substances has been investigated. A series-connected microbial fuel cell (MFC) stack is used to electro-reduce the CO_2 to formic acid in situ utilizing the electricity generated from the degradation of the carbonaceous substances in the anodic chambers of the MFC stack. Consequently, formic acid at 4.27 mg L^{-1} h^{-1} is produced, and a Faraday efficiency of 64.8% is achieved. This technology will be helpful in recycling and reusing the carbon in wastewaters or wastes in the absence of external energy input, thereby promoting the virtuous cycle of carbon.

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1. Introduction

The atmospheric concentration of CO_2 has been reported as 385 ppm (+37.5% compared with the pre-industrial level of 280 ppm) and is increasing at a rate of 2 ppm y^{-1} (0.52% y^{-1}) [1]. In the past, the global carbon cycle worked non-virtuously. Consequently, CO_2 has been accumulating in the atmosphere and acting as the leading cause of global warming. The processing of traditional wastewater, along with the degradation of organic pollutants, has released large amounts of CO_2 into the atmosphere. The global CO_2 emissions discharged from wastewater treatment plants could reach an estimated 1.21×10^4 t d^{-1} by 2025 [2]. Thus far,

sufficient attention has not been paid to CO_2 emissions from wastewater treatment facilities.

Various methods have been proposed for CO_2 sequestration, including physical adsorption [3,4], chemical absorption [4,5], bioconversion [6,7] and electrochemical reduction [8,9]. Of these methods, electrochemical reduction of CO_2 seems most promising because it consumes less energy than traditional chemical reduction processes and can proceed at a moderate temperature and atmospheric pressure [10]. In the electrochemical processes driven by direct-current power supplies, the final products of CO_2 reduction vary considerably with the metal cathodes used. The electrochemical reduction of CO_2 on a Pb electrode leads to an efficient and selective formation of formic acid [11–13]. Koleli et al. [11] reported the electrochemical reduction of CO_2 on Pb granules in an undivided fixed-bed reactor. Formic acid was detected as the predominant product, and the highest Faraday efficiency for formic acid formation was 94% at -1.8 V vs. SCE in 0.2 M K_2CO_3 solution. A higher Faraday efficiency of 97.4% could be achieved in 0.1 M $KHCO_3$

at -1.88 V vs. SCE [12]. However, the cost of the electricity consumed is still high.

Microbial fuel cell (MFC) is an emerging device that can generate electricity from the organic matter in domestic or industrial wastes and wastewaters [14]. Carbon dioxide is emitted from the MFC anodic chambers as the major gaseous end product [15]. Several research groups [16–18] have developed bio-cathode MFCs for CO_2 sequestration. By introducing the anodic off gas into an alga grown cathode, Wang et al. [18] built a new MFC-based device named microbial carbon capture cell (MCC) to realize CO_2 sequestration. Cheng et al. [16] demonstrated the feasibility of reducing CO_2 to CH_4 using a methanogen-containing cathode, and they reported relatively high electron-capture efficiencies of greater than 96%, respectively. However, CH_4 has a much higher global warming potential than CO_2, and its release will pose additional risks [19]. A promising long-term objective is to convert CO_2 to valuable chemicals, such as formic acid. Demand for formic acid for use in pharmaceutical syntheses, as well as in paper and pulp production, has been growing. The conversion of CO_2 to formic acid has therefore garnered considerable attention [11–13].

The literature contains no published accounts of MFCs being used as a power supply for the direct electrochemical reduction of CO_2. This dearth of research may be a consequence of the low reduction potential of CO_2 (-1.5 V vs. Ag/AgCl on a Pb electrode), and the limited output voltage of a single MFC cannot satisfy this voltage requirement. Even if the internal losses are neglected, the output voltage of a single MFC will never exceed a theoretical open-circuit voltage (OCV) of 1.14 V as determined by the redox potentials of NADH (-0.32 V) and pure oxygen ($+0.82$ V) [20]. MFCs can be connected in series, resulting in a nearly additive increase in total voltage [21]. Aelterman [20] reported that, with ferricyanide as the catholyte, the connection of six MFC units in series produced an OCV of 4.16 V. Sun et al. [22] employed several MFCs connected in series to supply power for a hydrogen-producing microbial electrolysis cell (MEC). The authors demonstrated that the serial connection greatly increased the input voltage of the MEC and thus led to a higher circuit current and hydrogen production rate. Hence, it is possible to complete the CO_2 reduction process powered by a series-connected MFC stack. If the dominant product of CO_2 in the MFC anodic chamber was collected and reduced to valuable chemicals with in-situ utilization of electricity generated by the MFC stack, an environmentally friendly method would be achieved for the recovery and utilization of carbon from wastes and wastewaters. Research toward this end has not been reported.

Here, we explore an environmentally friendly method to achieve the fixation of CO_2. An MFC stack was used to transform the chemical energy in the carbonaceous substances into electricity. The generated electricity was simultaneously utilized to reduce the CO_2 released from the degradation of the carbonaceous substance to formic acid. This exploration will be helpful to recycle and reuse the carbon in wastewaters or wastes in the absence of external energy input and thus to promote the virtuous cycle of carbon.

2. Materials and methods

2.1. MFC setup

Six MFCs were constructed, including five identical single-chambered MFCs ($5 \times 5 \times 5$ cm^3) and one two-chambered MFC (290 mL for each compartment). Carbon paper containing a Pt catalyst (0.5 mg cm^{-2}) on the water-facing side (Feichilvneng Co., Beijing, China) was used as the air cathode for all single-chambered MFCs, and it was connected to the external circuit by a copper mesh (100 mesh, Hiway Co., Beijing, China). Non-wet-proofed carbon fiber (3 mm thick, Beijing Evergrow Resources Co., Ltd., China) was

used as the anodes for all MFCs and the cathode for the two-chambered MFC. All electrodes used in the MFCs had a projected surface area of 16 cm^2. The electrode spacing was 2 cm in the single-chambered MFCs and 5 cm in the two-chambered. The two compartments for the two-chambered MFC were separated by a proton exchange membrane (PEM, Nafion117, 5 cm diameter, Dupont, USA). The PEM was sequentially boiled in H_2O_2 (30%), deionized water, H_2SO_4 solution (0.5 M) and again in deionized water (each for 1 h) and then immersed in deionized water for use [23]. Air was aerated continuously into the phosphate buffer solution (0.1 M) to supply O_2 as the electron acceptor for the cathodic chamber of the two-chambered MFC.

All MFCs were inoculated with anaerobic sludge (collected from Xiaojiahe Wastewater Treatment Plant in Beijing, China, 50% v/v) and fed with a synthetic medium. The medium compositions were prepared as follows (per liter): glucose, 800 mg; $NaH_2PO_4 \cdot 2H_2O$, 5620 mg; $Na_2HPO_4 \cdot 12H_2O$, 6150 mg; NH_4Cl, 310 mg; KCl, 130 mg; and a mineral solution of 12.5 mL [24]. The anodic chambers were refilled each time the voltage decreased to less than 50 mV. All reactors were operated with a fixed external circuit resistor (1000Ω) in fed-batch mode. An MFC stack was obtained by connecting the cathode of one MFC with the anode of an adjacent MFC using copper wire.

2.2. MEC setup

MEC was modified from the two-chambered MFC mentioned above by changing the cathode and the catholyte. A plate of Pb (4×4 cm^2, 99.9%, General Research Institute for Nonferrous Metals, Beijing, China) was used as the cathode of the MEC, and it was pretreated in H_2SO_4 solution (1 M) at room temperature for 10 min and then successively rinsed with acetone and ultra-pure water. A $KHCO_3$ solution (0.1 M) was used as the catholyte for CO_2 reduction.

2.3. Cylinder CO_2 electrolysis

Cylinder CO_2 was first electro-reduced by the MEC driven by the MFC stack. The MEC catholyte of $KHCO_3$ solution (0.1 M) was saturated with cylinder CO_2, and four methods were used for CO_2 electrolysis: 1) conventional electrolysis without any extra operations performed on the Pb electrode or the electrolyte in the process; 2) intermittent electrolysis with a regular surface cleaning of the Pb electrode with H_2SO_4 solution (1 M); 3) conventional electrolysis with aeration (successive CO_2 aeration in the electrolytic process); and 4) intermittent electrolysis with aeration. An electrolysis time of 240 min was applied for each batch, not including the time for cleaning the Pb electrode in the intermittent electrolysis process with or without aeration. The circuit current was measured from the voltage across a 10 Ω resistor connected in series with the MFC stack and the MEC.

2.4. Self-produced CO_2 electrolysis

Carbon dioxide produced by the MFC stack was collected for two cycles of electro-reduction. Nitrogen was successively bubbled into the anodic chambers of all MFCs to strip the produced CO_2 that was then absorbed with 20 mL of NaOH solution (2.5 M) in a slender tube. The CO_2 yield was reflected by the carbonate produced in the absorption process; the carbonate concentration was determined with a total organic carbon analyzer (Multi TOC/TN 3000, Analytik Jena AG, Germany). The CO_2-adsorbed solution was transferred to a flask in a water bath (80 °C), and excess H_2SO_4 solution (1 M) was injected dropwise into the NaOH solution to release CO_2. The released CO_2 was introduced and bubbled into the cathodic chamber of the MEC for electro-reduction. The $KHCO_3$ (0.1 M)

electrolyte was aerated with N_2 for 30 min to remove O_2 before the CO_2 was introduced. Intermittent electrolysis was chosen for this process.

2.5. Analysis and calculations

The output voltage (V) of the MFC stack was measured and recorded once every 10 min using a PMD-1608LS data acquisition unit (MCC Co., USA). The current (I) was calculated according to Ohm's law, $I = V/R$, where R was the known value of the external resistor. The power density (P) was calculated according to $P = VI/A$, where A was the projected area of the anode; here, A represents the sum of the anode areas for the MFC stack. To obtain the polarization and power density curves, the MFC stack was first run under open-circuit conditions for 2 h to achieve a steady OCV. The external resistors were then gradually decreased from 90,000–90 Ω with an interval of 2 h between the resistor changes.

Each batch of the electrolysis was repeated three times, and the average was used for data analysis. The products dissolved in the electrolyte, including formic acid, were analyzed by ion chromatography (Dionex ICS-900, AS23 column using 3.5 mM Na_2CO_3/ 1.0 mM $NaHCO_3$ as the mobile phase). The sampling was set at 0, 30, 60, 90, 120, 180 and 240 min from the start of electrolysis. The Faraday efficiency for the formation of formic acid (FE_{HCOOH}) was calculated as follows:

$$FE_{HCOOH} = \frac{n_{HCOOH} \times n \times F}{\int_0^t I \, dt} \times 100\%$$

where n_{HCOOH} is the moles of formic acid harvested; n represents the number of electrons required for the formation of one molecule of formic acid from CO_2 ($n = 2$ here); F is Faraday's constant (96,485 C/mol of electrons); and I is the circuit current.

The surface morphology of the Pb electrode was investigated by SEM (NOVA NANOSEM 430, FEI Co.).

3. Results and discussion

3.1. Characterization of MFC stack

Using cyclic voltammogram (data not shown), we found the optimal cathode potential for CO_2 reduction at a Pb electrode was −1.55 V vs. Ag/AgCl. To achieve a cathode potential negative enough for CO_2 reduction, MFC stacks were constructed by connecting MFC units in series. The effect of the number of MFC units on the cathode potentials of MEC is depicted in Fig. 1. An increased unit number tended to produce increasingly negative cathode potentials. Only the MFC stack that contained five units exhibited a cathode potential (−1.58 V vs. Ag/AgCl) sufficient to reduce CO_2 (−1.55 V vs. Ag/AgCl). Consequently, the MFC stack (with five series-connected MFC units unless otherwise noted) was chosen as the power supply for the CO_2 electrolysis. The performance of the MFC stack as a power supply was subsequently investigated, and the results are illustrated in Fig. 2. An OCV of 2.73 V was produced by the stack (0.564, 0.557, 0.557, 0.527, and 0.527 V for the five units, respectively). The maximum power density was 180 mW m^{-2} (at the current density of about 0.2 A m^{-2}). In detail, the maximum power densities for the five units were 142, 229, 203, 184, and 159 mW m^{-2}, respectively.

The output voltage variations of the MFC stack in two cycles are presented in Fig. 2b. The peak voltage was repeatable and equal to 1.13 and 1.14 V for the two cycles. The peak voltage lasted 4–5 h in each cycle. The MFC stack was consequently considered a reliable
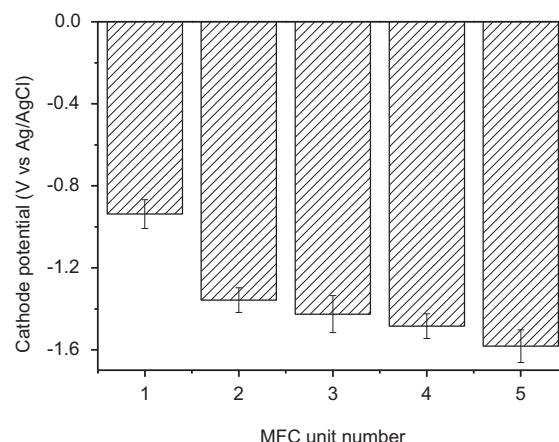

Fig. 1. Effect of the number of MFC units on the cathode potential of MEC.

power supply based on the stable and repeatable voltages it produced.

3.2. Cylinder CO_2 electrolysis

Formic acid has been reported to be the major product [11–13] of CO_2 reduction at a Pb cathode. In the present work, formic acid was measured by ion chromatography. In the process of cylinder
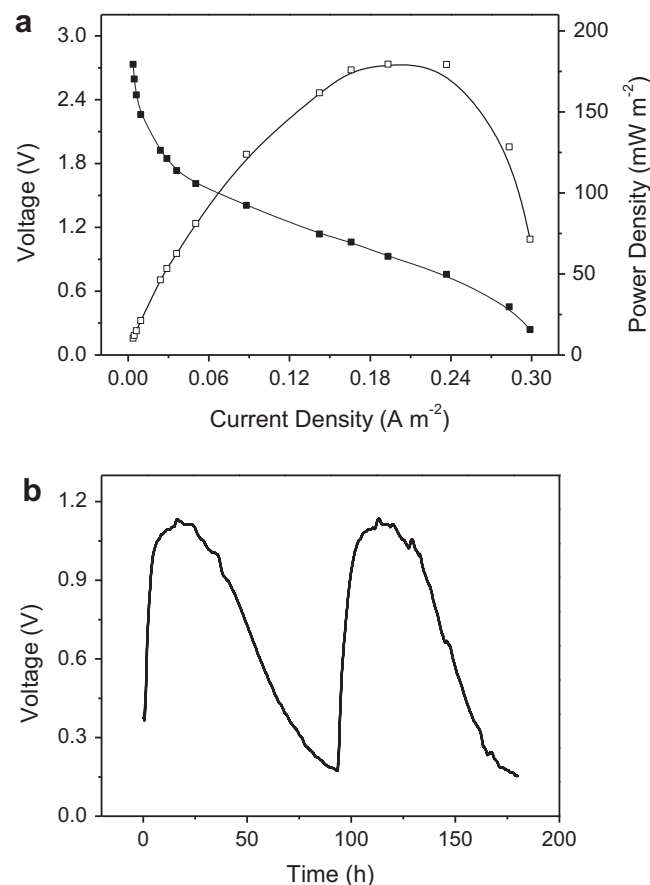

Fig. 2. Power-generation performance of the MFC stack with five series-connected MFC units: (a) polarization curve (■) and power density curve (□); (b) output voltage across a 1000 Ω resistor.

CO_2 electrolysis, the potential of formic acid production is reflected by the current produced by the MFC stack and applied to the MEC. The current variations with electrolysis time were firstly investigated, and the results are shown in Fig. 3. For conventional electrolysis, the current was initially 8.25 mA, but a sharp decline in the current was observed within the subsequent few minutes. The current dropped to 2.17 mA after an electrolysis time of 10 min and remained unchanged for the remaining duration of the electrolysis. This phenomenon was likely caused by the deactivation of the Pb electrode and the mass transfer of CO_2.

Intermittent electrolysis was used to investigate the effects of the Pb electrode deactivation. At electrolysis times of 30, 60, 90, 120 and 180 min, the Pb electrode was removed, inserted into a H_2SO_4 solution (1 M) for surface cleaning, and then reused to continue electrolysis. As exhibited in Fig. 3, an increase in the current was observed after each cleaning of the Pb electrode surface. Yet, the current dropped again soon thereafter, similar to the decrease observed during the conventional electrolysis. This effect may indicate the accumulation of poisoning species on the Pb electrode surface that deactivated the electrode. After the poisoning species were removed by the cleaning, a fresh Pb electrode surface was obtained, and thus the current increased again. Similar action was taken by Ogura [25], who used acidic solutions for the electrolysis process to avoid electrode deactivation.

The Pb electrode is prone to "poisoning" or "deactivation" during the electrolytic process [25]. To illustrate this point, the surface morphologies of the Pb electrodes were characterized by SEM (Fig. 4). Some small and uniform crystal grains with an average size of 200 nm were observed on the plain Pb electrode before electrolysis (Fig. 4a). After one batch of the conventional or the intermittent electrolysis, the grains grew in size, and the Pb electrode surfaces blackened (Fig. 4b and c). As a consequence of the surface cleaning of the Pb electrode with acid, the electrode surface in the intermittent electrolysis was brighter than that in the conventional electrolysis. These results demonstrate that some poisoning species (such as graphitic carbon or metal oxide) were accumulated on the Pb electrode surface during electrolysis. The deactivation of the Pb electrode is one of the factors that affect the CO_2 electrolytic process.

The electrochemical reduction of CO_2 is an interface reaction, and the dissolved CO_2 must move from the bulk solution toward

Fig. 4. SEM images of the plain Pb electrode (a) and the Pb electrodes after the conventional (b) and the intermittent (c) electrolysis.
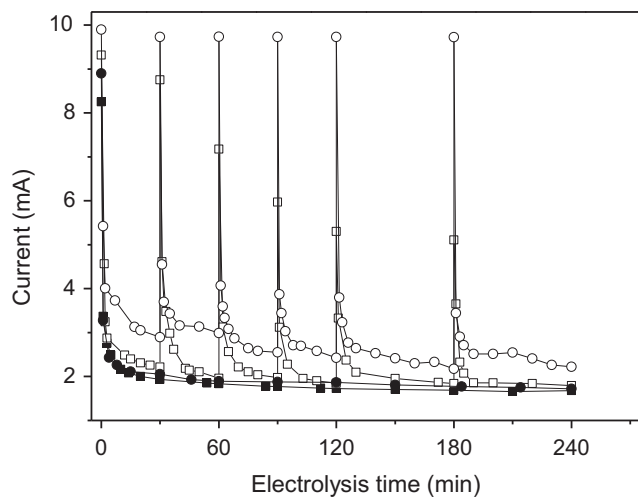

Fig. 3. Current variations with electrolysis time in the cylinder CO_2 electrolysis process: (■) conventional electrolysis; (□) intermittent electrolysis; (●) conventional electrolysis with aeration; (○) intermittent electrolysis with aeration.
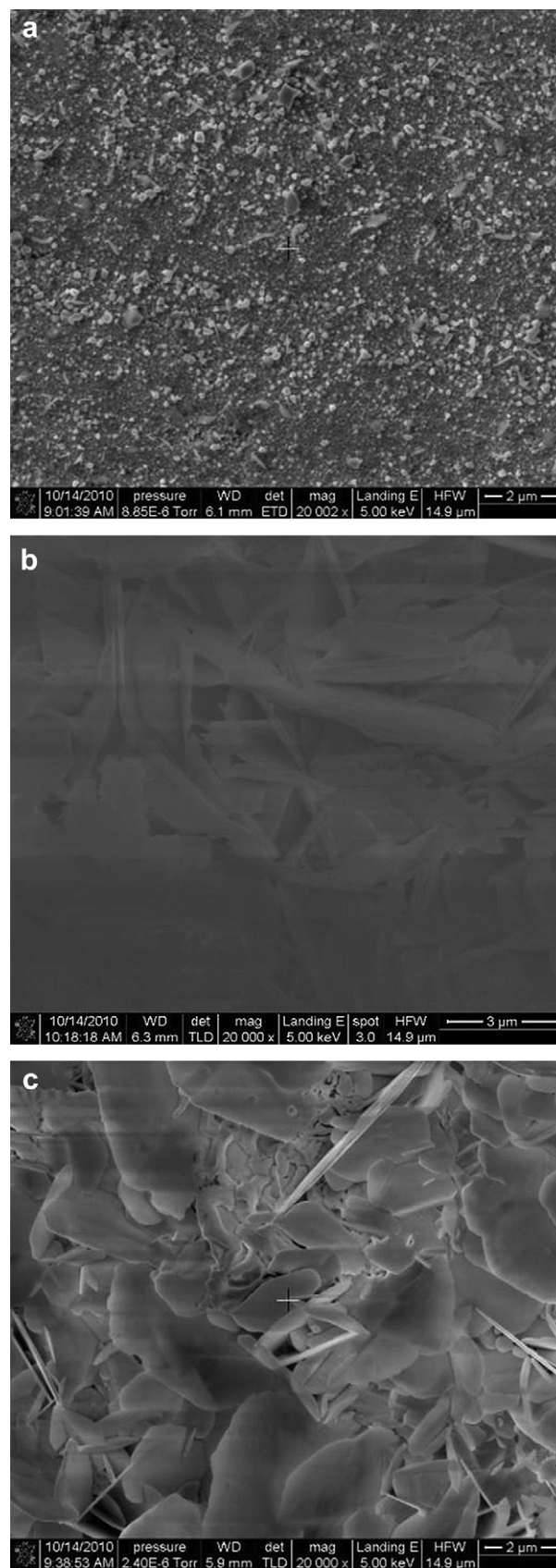
the electrode surface to accept electrons. To study the influence of the mass transfer of CO_2 on the reaction rate, successive CO_2 aeration was conducted for both the conventional and the intermittent electrolysis (Fig. 3). A comparison of the results indicates that the current with CO_2 aeration was slightly higher than the current without CO_2 aeration. Noticeably, as the intermittent electrolysis progressed, the maximum current measured under the conditions of clean and refreshed Pb electrode surfaces remained unchanged for the system with aeration but gradually declined for the system without aeration (Fig. 3). These results indicate that successive CO_2 aeration not only provided more CO_2 for the reaction but also increased the turbulences of the electrolyte, which resulted in an excellent mass transfer of CO_2. Collectively, these results indicate that successive CO_2 aeration is significant for the electrolytic process.

Based on the analysis of the electrolysis products, the formic acid production rate and the corresponding Faraday efficiencies during different electrolysis methods are illustrated in Fig. 5. As shown in Fig. 5a, the concentrations of formic acid increased with electrolysis time, irrespective of the applied electrolysis method. The intermittent electrolysis led to a higher concentration of formic acid than the conventional electrolysis because regular surface cleaning of the Pb electrode effectively mitigated the deactivation

and resulted in a relatively high reaction rate. The successive CO_2 aeration also promoted an increase in the formic acid concentration because excellent mass transfer of CO_2 was induced. Hence, the maximum production rate of formic acid (6.86 mg L^{-1} h^{-1}) was achieved at the electrolysis time of 240 min for the intermittent electrolysis with aeration. Moreover, the intermittent electrolysis without aeration produced more formic acid than the conventional electrolysis with aeration. The deactivation of the Pb electrode is apparently more dominant than the mass transfer of CO_2 in limiting the electrolytic process.

The Faraday efficiency for the formation of formic acid in the electrolytic process represents the ratio of the mass of formic acid liberated by a current to the theoretical mass, as predicted by Faraday's law. The Faraday efficiency is a key factor in the evaluation of the effects of side reactions and current leakage, among others. The Faraday efficiencies under the four electrolysis methods are illustrated in Fig. 5b. For the conventional electrolysis, the Faraday efficiencies decreased with electrolysis time, whereas the Faraday efficiencies remained basically unchanged during intermittent electrolysis. The methods that involved aeration slightly increased the Faraday efficiencies compared to those that did not involve aeration. Hence, in the intermittent electrolysis process with aeration, the Faraday efficiency reached a maximum of 70.0%. The related literature for CO_2 reduction (Pb electrode) indicates that the Faraday efficiencies range from 44% to 97.4%, and all of the reported electrolytic processes were driven by direct-current power supplies [11–13]. The maximum Faraday efficiency obtained in the present work was relatively high, despite the power being supplied by an MFC stack. These results indicate that the MFC stack in the present experiment worked efficiently (as expounded in Fig. 2) and was able to serve as an equivalent of an external power supply.

3.3. Self-produced CO_2 electrolysis

Attempts were made to electro-reduce the CO_2 produced in the anodic chambers of the MFC stack using the simultaneously generated electricity. After being collected for two cycles, a measured amount (12.7 mmol) of CO_2 was introduced to the cathodic chamber of the MEC for reduction. Because the solubility of CO_2 in aqueous solutions is on the order of 30 mM at 298 K, the amount of CO_2 collected was sufficient for the test in which only 250 mL of electrolyte (0.1 M $KHCO_3$) was used. The intermittent method was chosen for the self-produced CO_2 electrolysis, and the results are shown in Fig. 6. The currents exhibit a trend (Fig. 6a) similar to that observed in the intermittent electrolysis without cylinder CO_2 aeration (Fig. 3). The maximum formic acid production rate and the corresponding Faraday efficiency reached 4.27 mg L^{-1} h^{-1} and 64.8% (Fig. 6b), respectively, which is comparable to the results in the intermittent electrolysis without aeration (4.31 mg L^{-1} h^{-1} and 65.3%, Fig. 5). Therefore, it is feasible to electro-reduce the MFC-produced CO_2 in the MFC-stack-driven MEC.

In the present work, the CO_2 produced in the anodic chambers of the MFC stack was successfully reduced to formic acid in the cathodic chamber of the MEC using the simultaneously generated electricity without any external energy input. In the organic wastewater or waste-treatment processes based on MFCs, biological electricity would be generated while the organic matter was degraded to produce CO_2 [26,27]. If the device and the approach presented in this paper were optimized on a large scale and the MFCs were fed with organic wastewater or wastes, the CO_2 generated during wastewater processing and waste treatment can be converted into valuable chemicals (formic acid in this case)
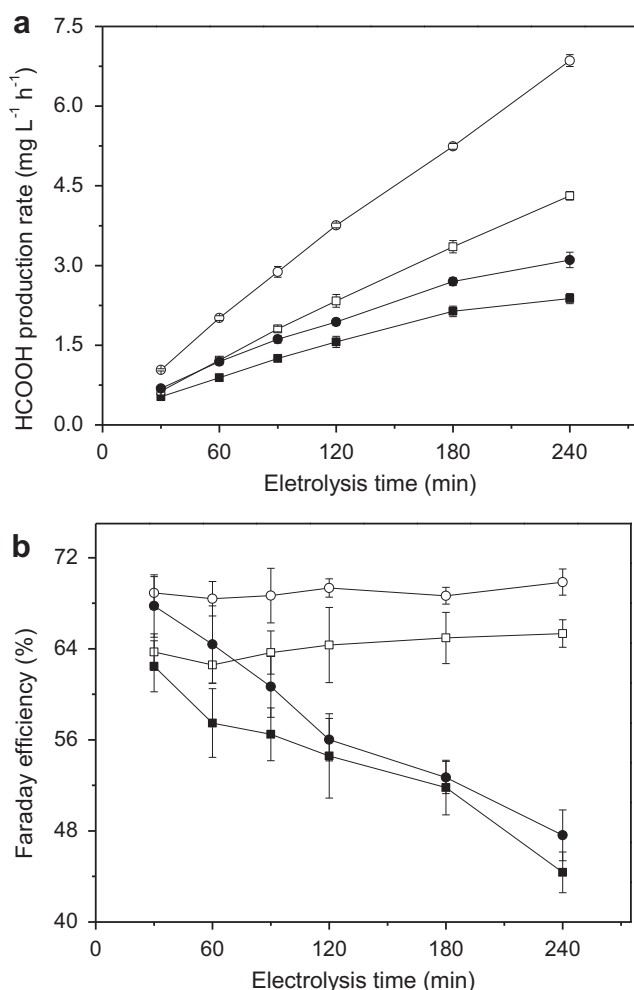

Fig. 5. Variations in the formic acid production rate (a) and the Faraday efficiency (b) with electrolysis time in the cylinder CO_2 electrolysis process: (■) conventional electrolysis; (□) intermittent electrolysis; (●) conventional electrolysis with aeration; (○) intermittent electrolysis with aeration.
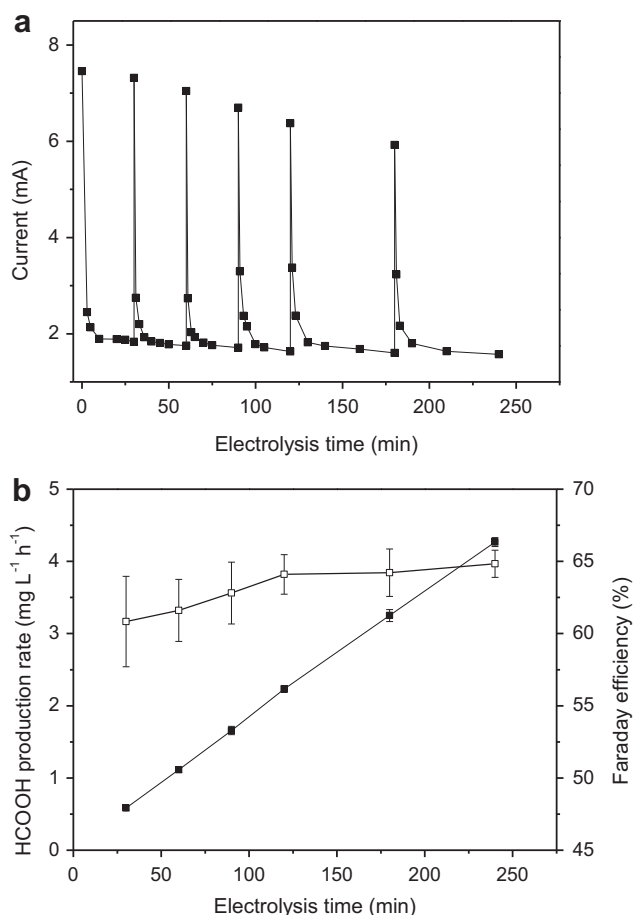
Fig. 6. Variations in the current (a), the formic acid production rate (b, ■) and the Faraday efficiency (b, □) with electrolysis time in the self-produced CO_2 electrolysis process.

without any external energy input. Hence, a virtuous carbon cycle can be achieved.

4. Conclusions

MFC-produced CO_2 was successfully reduced to formic acid in the MFC-stack-driven MEC without any external energy input. The required potential for CO_2 reduction was investigated by cyclic voltammetry and determined to be −1.55 V vs. Ag/AgCl. To satisfy the requirements of the cathode potential, five single-chambered MFCs were connected in series to construct an MFC stack to serve as the power supply. Consequently, a cathode potential of −1.58 V vs. Ag/AgCl was reached for the MEC. The stack was stable and

repeatable when operated, and its OCV and the maximum power density reached 2.73 V and 180 mW m^{-2}, respectively. For the cylinder CO_2 electrolysis, the highest formic acid production rate and the highest Faraday efficiency were 6.86 mg L^{-1} h^{-1} and 70.0% respectively. Both the deactivation of the Pb electrodes and the mass transfer of CO_2 influence the electrolytic process, and the deactivation process is dominant. For the self-produced CO_2 electrolysis, formic acid at 4.27 mg L^{-1} h^{-1} was produced, and a Faraday efficiency of 64.8% was achieved. It is feasible to electro-reduce the MFC-produced CO_2 in situ using the electricity generated by the MFC.

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